

The invention relates to a method of fabricating membrane-electrode assemblies, particularly for PEM fuel cells, which comprise catalytically active electrodes.

Fuel cells are energy converters that convert chemical energy into electrical energy. In a fuel cell, the electrolytic principle is inverted. Nowadays, various types of fuel cells are known which generally differ from one another with respect to their operating temperature. The design of the cells, however, is in principle the same for all types. They generally comprise two electrodes, an anode and a cathode, at which the reactions proceed, and an electrolyte between the two electrodes. In the case of a polymer-electrolyte membrane fuel cell (PEM fuel cell) the electrolyte used is a polymer membrane which conducts ions (especially H^+ ions). The electrolyte has three functions. It establishes the ionic contact, prevents electrical contact, and additionally ensures that the gases fed to the electrodes are kept separate. As a rule, the electrodes are supplied with gases which are reacted as part of a redox reaction. The electrodes have the functions of feeding in the gases (e.g. hydrogen or methanol and oxygen), of removing reaction products such as water or CO_2 , of catalytically reacting the starting materials and of drawing off or supplying electrons. The conversion of chemical into electrical energy takes place at the three-phase boundary of catalytically active sites (e.g. platinum), ion conductors (e.g. ion exchange polymers), electron conductors (e.g. graphite) and gases (e.g. H_2 and O_2). Crucially, the catalysts should have as large an active surface area as possible.

In the prior art, the fabrication of PEM fuel cells usually involves mixing a catalyst supported on carbon black with a solution or suspension of an ion conductor (ionomer) and applying the mixture to the ion-conducting membrane. This has the drawback of not ensuring that the catalyst present on the electron conductor will

indeed have been made completely accessible by the ion conductor and thus be able to be active.

Moreover, high (cost-intensive) catalytic loading is often required, owing to non-optimal catalyst utilization. This is due to the fact that a large proportion of the catalysts applied over the entire area of the membrane remains virtually unutilized, since a proportion of the catalysts is not made accessible by the ionomer and the ion conduction in the membrane usually does not take place over its entire area, but e.g. via ion channels resulting from phase separation, or via pores of a non-conductive polymer which are filled with an ion conductor. Catalyst atoms located at the ends of such channels are able to take a particularly effective part in the electrochemical reaction. In addition, in fabricate-reinforced or heterogeneous membranes regions will be formed which take no part in ion transport and consequently shield a proportion of the catalysts present in the electrode. That fraction of the catalyst which is consequently not utilized contributes to the excessive costs of such a fuel cell.

The attempt to systematically locate the catalysts solely in the electrochemical reactive zones is disclosed by US 5 084 144. With this method of enhancing the electrocatalytic activity of a gas diffusion electrode, a catalytic metal is electrolytically deposited on the gas diffusion electrode *from an electrolytic fluid*. The catalytic metal is therefore not deposited systematically solely at the ends of the ion channels of the membrane, but over the entire area. A further drawback of this method is that expensive electrolytic fluids containing noble metals are required, which are laborious and expensive to work up. Moreover, the utilization of the noble-metal catalyst dissolved in the electrolyte is low. Furthermore, the electrolyte fluid usually contains not just the desired catalytic ions, but also other ions which are deposited on the gas diffusion electrode and which represent contaminants of the deposited catalyst layer.

A method of electrolytically depositing metals on a solid electrolyte is disclosed by DE-A 28 21 271, wherein the solid electrolyte, in the dried state, treated in a solution containing the metal as a salt, is inserted into an electrolytic cell and is subjected to an electrolytic process. In so doing, the cell is kept at a constant current density over a predetermined period. This results in a continuous surface cutting of this electrolyte, which means that catalyst atoms are present not only at those sites

which are catalytically active under fuel cell conditions, but on the entire solid electrolyte surface.

5 It is therefore an object of the present invention to provide a method by which optimal catalytic loading is achieved on the electrodes of a PEM fuel cell.

This object is achieved by a method of fabricating a membrane-electrode assembly (MEA), particularly for PEM fuel cells, wherein the MEA comprises a polymer-electrolyte membrane (PEM) with reaction layers applied to both sides and possibly with gas distribution layers, and at least one of the reaction layers includes at least one catalytic component and an electron conductor, the method comprising the following procedural steps:

15 A) The introduction of ions of the at least one catalytic component into the polymer-electrolyte membrane and/or into an ionomer introduced into the reaction layers,

20 B) the application of the electron conductor to both sides of the polymer-electrolyte membrane,

C) the electrochemical deposition of the ions of the catalytic component from the polymer-electrolyte membrane and/or from the ionomer, introduced into the reaction layers, on the electron conductor onto at least one side of the polymer-electrolyte membrane.

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The polymer-electrolyte membrane in the context of the present invention is to be understood as meaning either a polymer membrane serving as the electrolyte or a polymer membrane whose pores are filled with a substance serving as an electrolyte (e.g. with an ionomer, acid).

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The at least one membrane-electrode assembly (MEA), composed of the components electrode/membrane/electrode arranged like a sandwich, represents the central element of the PEM fuel cell. A PEM fuel cell usually comprises a stack-like arrangement of a multiplicity of membrane-electrode assemblies. Each electrode usually comprises a reaction layer and, in the case of fuel cells that run on gases, a gas distribution layer.

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The gas distribution layer can serve as a mechanical support for the electrode and ensures that the respective gas is properly distributed across the reaction layer and that the electrons are collected. A gas distribution layer is required, in particular, for fuel cells operating with hydrogen on the one hand and oxygen or air on the other hand.

The reaction layer is where the electrochemical reaction proper takes place during fuel cell operation. At least one of the reaction layers contains at least one catalytic component which catalytically supports e.g. the reaction of oxidation of hydrogen or of reduction of oxygen. Alternatively, however, the reaction layers may contain a plurality of catalytic substances having different functions. In addition, the reaction layer may contain a functionalized polymer (ionomer) or a nonfunctionalized polymer.

Further, an electron conductor in the reaction layers serves, inter alia, to conduct the electric current which flows during the fuel cell reaction, and as a support material for catalytic substances.

To implement the method according to the invention, ions of a catalytic component are first of all introduced into the polymer-electrolyte membrane. In the same way, the ions can additionally be introduced into the ionomer which may, if required, have been incorporated into the reaction layer.

The polymer-electrolyte membrane consists of cation-conductive polymer materials which hereinafter are referred to as ionomer. Customarily, a tetrafluoroethylene-fluorovinyl ether copolymer having acid functions, especially sulfuric acid groups, is used. Such a material is commercially available, for example, under the trade name Nafion® by E.I. du Pont. Examples of ionomer materials that can be used in the present invention are the following polymer materials or mixtures thereof:

- Nafion® (Dupont; USA)
- perfluorinated and/or partially fluorinated polymers such as "Dow experimental membrane" (Dow Chemicals, USA),
- Aciplex-S® (Asahi Chemicals, Japan)
- Raipore R-1010 (Pall Rai Manufacturing Co., USA),
- Flemion (Asahi Glass, Japan)

- Raymion® (Chlorine Engineering Corp., Japan).

Alternatively, however, other, especially fluorine-free, ionomer materials can be used, e.g. sulfonated phenol formaldehyde resins (linear or crosslinked); sulfonated polystyrene (linear or crosslinked); sulfonated poly-2,6-diphenyl-1,4-phenylene oxides, sulfonated polyarylethersulfones, sulfonated polyarylethersulfones, sulfonated polyaryletherketones, phosphonated poly-2-6-dimethyl-1,4-phenyl oxides, sulfonated polyetherketones, sulfonated polyetheretherketones, arylketones or polybenzimidazoles.

In addition, those polymer materials are used which include the following components (or mixtures thereof):

Polybenzimidazol-phosphoric acid, sulfonated polyphenylenes, sulfonated polyphenylene sulfide and polymeric sulfonic acids of the type polymer-SO₃X (X = HH₄⁺, NH₃R⁺, NH₂R₂⁺, NHR₃⁺, NR₄⁺).

In addition to the above-listed polymer materials, the ion exchange materials used may include further inorganic and/or organic components (e.g. silicates, minerals, clays, silicones) which have a positive effect on the properties of the ionic exchange material (e.g. conductivity).

Also possible is the use of porous non-conductive polymers which require their conductivity by the pores being filled with e.g. an ionomer (for example Goreselect, Gore, USA) or an acid (for example H₃PO₄, H₂SO₄, methanesulfonic acid, ...).

The introduction of the ions of a catalytic substance into the polymer-electrolyte membrane is effected by a technique known in the prior art. Preferably, the catalytic substance is present ionically in a solution with which the polymer-electrolyte membrane is impregnated. In the process, ion exchange causes the ions of the catalytic substance to bind to the membrane, e.g. in Nafion® to bind to ionic SO₃H groups.

In the case of acid-filled membranes, it is possible to mix the acid with the catalytic substance for the purpose of introducing the ions of the catalytic substance into the membrane.

In one embodiment of the present invention, the diffusion of the ions of the catalytic substance into the polymer-electrolyte membrane is promoted by an external electric field being applied.

5 The next step B) in the method according to the invention is the application of the electron conductor to both sides of the polymer-electrolyte membrane. This purpose can be served by a technique known in the prior art, for example a dry or wet spray technique with the aid of which the electron conductor present as a powder or possibly dissolved in an ionomer solution is sprayed directly onto the membrane
10 or onto a support, followed by optional hot compression bonding to the membrane. Further options of applying include e.g. screen printing or sintering followed by optional hot compression-bonding to the membrane. Also conceivable is the introduction of ions of the catalytic component into an ionomer incorporated into the electron conductor layer.

15 Prior to the next step C) of the method according to the invention, the at least one membrane-electrode assembly is largely finished and installed in an apparatus which allows an electric current to be impressed or reactants (e.g. H_2/O_2) to be fed in while at the same time an electric current is tapped off. Also conceivable would
20 be a continuous procedure, in which step C) of the method according to the invention is carried out, and the at least one membrane-electrode unit as processed is then installed in a PEM fuel cell.

In the membrane-electrode assembly installed, prior to step C), in a PEM fuel cell
25 or in another apparatus suitable for performing the electrochemical deposition, the catalytic substance introduced into the membrane in step A) is present in the form of ions bound within the membrane (for example to its negatively charged sulfone groups). These are deposited electrochemically, in step C) of the method according to the invention, from the polymer-electrolyte membrane onto the electron conduc-
30 tor on at least one side of the polymer-electrolyte membrane. The electrochemical deposition is to be understood, in this context, as the deposition of the catalytic components while chemical energy is converted into electrical energy or vice versa, the mechanism being ion migration within the membrane and an electrode reaction taking place.

35 An advantage of the method according to the invention is that as a result of the electrochemical deposition of the catalytic component from the membrane, said

catalytic component can be deposited only where the electrochemically active three-phase boundary is also present. The catalytic component is therefore deposited specifically onto the electron conductor in those locations where the ion channels of the membrane terminate. As a result, a continuous layer of the catalytic component is not formed, the catalyst instead being deposited only at those plates where it is optimally utilized. The result is an effective reduction in catalytic loading without a decrease in the fuel cell performance. For example it is possible to operate fuel cells having a Pt loading of the electron conductor of less than 1 mg/cm². The reduction in the catalytic loading advantageously means a cost reduction for MEA fabrication, since the catalytic components used are often metals. Since the catalytic component in the present invention is present in finely dispersed form as ions in the interior of the polymer-electrolyte membrane, another point is that, in contrast to the deposition of catalyst ions from a solution, with the method according to the invention no impurities in the form of other undesirable ions are deposited on the electron conductor, but only the catalyst ions present in the membrane. A further advantage of the method according to the invention is the small number of procedural steps for fabricating a polymer-electrolyte membrane fuel cell. This too has a positive effect on costs. These possible cost reductions make the use of PEM fuel cells more attractive for wired commercial use, for example in fuel cell vehicles or in stationary fuel cell systems for domestic power supplies.

In a preferred embodiment of the present invention, the electrochemical deposition of the ions of the catalytic component in step C) of the method according to the invention is effected by operating an apparatus which allows an electrical current to be tapped off and fuel cell reactants to be fed in under fuel cell conditions, e.g. by operating a PEM fuel cell on the fuel conditions. By varying the operating conditions during the deposition (load cycle, current, voltage, gas composition, temperature, pressure etc.) it is possible for the result of the deposition (dispersity, particle size) to be systematically controlled.

If the electrochemical deposition is carried out e.g. under H₂/O₂, air fuel cell conditions, gas distribution layers are required which must be applied to the reaction layers or to the respective electron conductor before step C) of the method according to the invention is carried out. The gas distribution layers (for example bonded carbon fiber web (E-Tek carbon cloth) or carbon paper (e.g. Toray carbon paper (Electrochem. Inc.), Spectracorp carbon paper (Spectracorp), Sigracet Gas Diffusion Media (SGL Carbon))) are applied, prior to the electrochemical deposition

- (step C)) by laying on, rolling, hot pressing or other techniques known to those skilled in the art. Then the anode of the apparatus is fed with e.g. hydrogen and the cathode is fed with e.g. oxygen. At the anode, which preferably already includes a catalyst which lowers the activation energy for this reaction, H^+ ions and electrons are produced by oxidation of the hydrogen. The H^+ ions, together with the ions of the catalytic component introduced into the membrane in step A) migrate through the membrane to the cathode which preferably already includes a small amount of the catalytic component and at which the reduction of oxygen to water and the deposition of the catalyst cations takes place. The electrons required for the reduction flow through an external electric circuit from the anode to the cathode. Thus the catalyst cations are advantageously, without an additional procedural step, deposited at precisely those locations on the electron conductor so as to be firmly attached thereto, where they are optimally utilized for the fuel cell.
- 15 Alternatively, electrochemical deposition of the at least one catalytic component onto the electron conductor in a liquid milieu is possible, for example in a direct-oxidation fuel cell such as a direct-methanol fuel cell.

In a further preferred embodiment of the present invention, the electrochemical deposition of the ions of the catalytic component in step C) of the method according to the invention is effected by operating an apparatus which allows an electric current to be impressed for the electrolytic deposition of the catalytic component. This is done, for example, by operating the apparatus (e.g. a PEM fuel cell) under electrolytic conditions. Once the membrane-electrode assembly prior to step C) of the method according to the invention has been largely finished and been installed in the apparatus (e.g. a PEM fuel cell), the ions present in the membrane are deposited electrolytically on the electron conductor. The catalyst ions thus deposited are located precisely as targeted at the end of ion-conducting regions of the membrane and are thus wholly active. The electrolysis can be fed out by a DC voltage being applied to the electrodes of the apparatus (e.g. fuel cell). As a result, the metal ions which are present in uniform dispersion in the polymer-electrolyte membrane, are deposited cathodically on the electron conductor. Depending on which electron conductor (on the anode or cathode side of the fuel cell) the catalytic component is to be deposited on, the polarity of the electrodes during the electrolysis is chosen accordingly.

In a preferred embodiment of the present invention, the electrolysis for depositing the catalytic component is carried out by applying a time-variant, e.g. pulsed DC voltage or a time-variant DC current to the electrodes of the fuel cell, with the resultant advantage that control of the particle size of the deposited particles and of the surface morphology of the catalyst (e.g. the noble metal) becomes possible.

In a further preferred embodiment of the present invention, the electrolysis for depositing the catalytic component from the membrane onto the respective electron conductor is carried out by applying an AC voltage (alternatively a DC voltage whose polarity is periodically reversed) or a DC voltage with an AC voltage superimposed thereon to the electrode in the fuel cell. With this procedure, the catalytic component can continue to be deposited alternately on the two electrodes. This has the advantage that the catalyst ions are deposited uniformly and in very finely dispersed form on both electrodes.

In a preferred embodiment of the present invention, in step C) at least one element from the 3rd to 14th group of the periodic table of the elements (PTE), equally preferably from the 8th to 14th group of the PTE is deposited as the catalytic component onto the electron conductor on at least one side of the polymer-electrolyte membrane. These electrocatalysts promote the fuel cell reaction (oxidation of hydrogen or reduction of oxygen) catalytically. As a result of the method according to the invention, these catalytically active components are applied in highly dispersed form to the surface of the electron conductor serving as a support. The abovementioned catalytically active components are introduced into the polymer-electrolyte membrane, in step A) of the method according to the invention, in a concentration of preferably 0.000005 to 0.05 mmol/cm².

In a preferred embodiment of the present invention, in step C) at least one of the elements Pt, Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Ir or W is deposited as the catalytic component on the cathode-side electron conductor in the fuel cell. While this is done, a further catalytic substance required for lowering the activation energy for the fuel cell reaction may already be present on the electron conductor. For example, in step C) of the method according to the invention, copper can be deposited as a second catalytically active substance on an electron conductor which already supports platinum as the first catalytically active substance. The abovementioned catalytically active components Pt, Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Ir or W to be deposited on the cathode side of

the fuel cell are introduced, in step A) of the method according to the invention, into the polymer-electrolyte membrane in an amount/concentration of preferably 0.000005 to 0.05 mmol/cm².

5 It has been found that there are problems, under fuel cell operating conditions, with the cathodic reduction of oxygen:

At cathodic electrode material of the fuel cell as described in the prior art, highly reactive peroxidic oxygen species (e.g. HO•, HOO•) are formed which cause irreversible damage to the proton-permeable membrane and the ionomer of the electrode. It was found that additives which have deperoxidation-active properties and are specifically introduced into or at the electrode material produce a sustainable increase in the lifetime or service life and economic efficiency of fuel cells. Here, the term deperoxidation-active is to be understood as the property of preventing the formation of peroxides and the retrospective decomposition of peroxides as already formed. Peroxides in this context are all compounds of type R-O-O-R and the corresponding free radicals (RO• or ROO•), where R is preferably H. For example, HOO• is a peroxidic radical corresponding to H₂O₂ (hydrogen peroxide). As a result of disposing suitable deperoxidation-active compounds and/or elements in or on the fuel cell electrodes, rapid breakdown of the peroxides or suppression of formation of peroxides is achieved under fuel cell conditions. Irreversible damage to the ionic exchange membranes by reactive peroxides is no longer observed. This is surprising, since according to the principle of microreversibility those substances which decompose peroxides are also able to form peroxides. For example, platinum under fuel cell conditions acts as peroxide former owing to the permanent O₂ supply. Under different conditions it is used for the decomposition of peroxide. Only by introducing further deperoxidation-active additives is it possible to decompose the peroxides formed on the platinum in the fuel cell or to inhibit their formation. The active components to be mentioned for such elements or compounds acting as deperoxidation-active additives are primarily the metals Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Ir or W. The said metals are therefore deposited as catalytic components, preferably by means of the method according to the invention, on the cathode-side electron conductor. They are introduced, in step A) of the method according to the invention, into the polymer-electrolyte membrane in an amount/concentration of preferably 0.000005 to 0.05 mmol/cm².

Another important object of fuel cell fabrication is the reduction of cathode-side overpotentials. Progress in this respect is achieved by catalysts comprising a plurality of active components. In a preferred embodiment of the present invention, a plurality of catalytic components are therefore deposited on the electron conductor on the cathode side in the fuel cell. In so doing it is possible, on the one hand for a plurality of catalytic components, in step A) of the method according to the invention, to be introduced into the polymer-electrolyte membrane (PEM), which are then, in step C), jointly deposited on the electron conductor, and/or, on the other hand, where components that are already catalytic to be applied together with the electron conductor onto the PEM in step B), followed by the deposition thereonto, in step C) of additional catalytic components.

In a preferred embodiment of the present invention, in step C) at least one of the elements Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Ir or W is deposited as the catalytic component on the anode-side electron conductor in the fuel cell.

In the course of "cold combustion" of methanol in the fuel cell, a byproduct formed in small amounts is carbon monoxide (CO). This results in an increase in the CO concentration on the anode side of the fuel cell, and a catalytic component (e.g. platinum) which serves to promote the anode reaction catalytically, is consequently loaded with CO. In H₂O₂ fuel cells, for which the hydrogen is supplied by hydrocarbon reformation, CO is likewise introduced into the fuel cell. In both cases, the free surface area of the catalytic component for H₂ adsorption and oxidation is therefore reduced, resulting in "CO poisoning" of the fuel cell. Via oxidation of the CO on the CO-loaded catalyst by H₂O it is possible to effect a "desorption" of the CO molecules. Base cocatalysts, e.g. ruthenium, allow H₂O to be absorbed at lower anode potentials, thus contributing to an increase in the CO tolerance on the anode side of the fuel cell. According to the invention, such catalytic components can be deposited precisely on target on the electron conductor on the anode side, for example ruthenium on a Pt-C electron conductor, thereby reducing the risk of CO poisoning of the fuel cell. The abovementioned components Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Pt, Ir or W to be deposited on the anode side of the fuel cell are introduced, in step A) of the method according to the invention, into the polymer-electrolyte membrane in an amount/concentration of preferably 0.000005 to 0.5 mmol/cm².

In the method according to the invention, the electron conductor used preferably contains at least one metallic element in the form of bonded fiber web, fibers or powder. Also conceivable is the use of electron-conducting polymers as electron conductors. Particular preference is given to the use of finely dispersed C blacks or graphite powders as electron conductors. In the fuel cell, the carbon black or the graphite, by means of the large surface area of their particles, serve as electrically conductive gas-porous supports for at least one catalytic component. By means of the method according to the invention, said catalytic component can be applied to the electron conductor which has previously been bonded to a polymer-electrolyte membrane.

In a preferred embodiment of the present invention, the electron conductor applied in step B) of the method according to the invention comprises at least one catalytic component from the group consisting of Pt, Co, Fe, Cr, Mn, Cu, V, Ru, Pd, Ni, Mo, Sn, Zn, Au, Ag, Rh, Ir or W. Here, the electron conductor, when it is bonded in step B) to the membrane, already serves as a support for at least one catalytic component (e.g. platinum), and at least one further catalytic component (e.g. Ru or Cu) or the catalytic component already present (e.g. additional Pt) is deposited, in step C) of the method according to the invention, on said catalyst-containing electron conductor. Thus it is possible, in the method according to the invention, for e.g. a catalytic component which enhances CO tolerance to be deposited on the anode side onto an electron conductor on which a catalytically active component which catalytically promotes the fuel cell reaction is already present. On the cathode side, for example, a deperoxidation-active component can be deposited on an electron conductor/catalyst combination.

In a preferred embodiment of the present invention, in step B), together with the electron conductor, an ion conductor (e.g. an ionomer solution or suspension) is applied to at least one side of the polymer-electrolyte membrane. The joint application of ionomer and electron conductor advantageously results in the electron conductor being made accessible to a high degree by means of ionomer, which means a large 3-phase interface area.